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**[Title of the Invention]**

Method for manufacturing a member provided with catalysts containing metal fine particles

**[Abstract]**

**[Object]** It is an object of the present invention to provide a decolorizing method for maintaining highly photo-catalytic activity without deteriorating a design of a base member such as colors or patterns.

**[Structure]** A method for manufacturing a member provided with catalysts containing metal fine particle, comprising the steps of immobilizing particles having photo-catalytic activity and colored metal fine particles on a base member and forming achromatized (colorless) or whitened salt on at least surfaces of the metal fine particles through reaction between said metal fine particles and a solution or a gas.

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**[What is claimed is:]**

**[Claim 1]** A method for manufacturing a member provided with catalysts containing metal fine particles, comprising the steps of:

fixing particles having photo-catalytic activity and colored metal fine particles on a base member; and

forming achromatized or whitened salt on at least surfaces of the metal fine particles through reaction between said metal fine particles and a solution or a gas.

**[Claim 2]** A method for manufacturing a member provided with catalysts containing metal fine particles, comprising the steps of:

fixing particles having photo-catalytic activity and colored metal fine particles on a base member; and

forming achromatized or whitened salt on at least surfaces of the metal fine particles through reaction between said metal fine particles and a solution or a gas, wherein the above steps are conducted in the sequence as mentioned above.

**[Claim 3]** A method for manufacturing a member provided with catalysts containing metal fine particles, comprising the steps of:

forming achromatized or whitened salt on at least surfaces of metal fine particles through reaction between metal fine particles and a solution or a gas; and

fixing particles having photo-catalytic activity and the metal fine particles, the surfaces of which are provided with the achromatized or whitened salt on a base member, wherein the above steps are conducted in the sequence as mentioned above.

**[Claim 4]** The method for manufacturing a member provided with catalysts containing metal fine particles according to claims 1 to 3, wherein the solution caused to react on said metal fine particles is a solution containing a material which forms the achromatized or whitened salt which is insoluble or hard to solve on at least the surfaces of the colored metal fine particles.

**[Claim 5]** The method for manufacturing a member provided with catalysts containing metal fine particles according to claims 1 to 3, wherein the solution caused to react on said metal fine particles comprises at least one kind of material which is selected from a halogenated salt solution such as ferric chloride aqueous solution or a solution containing an oxidizing agent such as hydrogen peroxide water or ozone water.

**[Claim 6]** The method for manufacturing a member provided with catalysts containing metal fine particles according to claims 1 to 3, wherein the gas caused to react on said metal fine particles comprises an oxidizing agent such as oxygen, water vapor or ozone.

**[Claim 7]** The method for manufacturing a member provided with catalysts

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containing metal fine particles according to claim 6, wherein the achromatized or whitened salt formed on at least the surfaces of the metal fine particles by being caused to react on the gas is insoluble or hard to solve.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

The present invention relates to a method for forming a mixture layer of metal particles and photo-catalyst which has an effect such as an antibacterial action, a deodorizing action or an anti-fouling action on a surface of a tile, a glass (e.g. a mirror), sanitary ware or a resin plate while maintaining its base color or design such as patterns.

[0002]

[Prior Art]

In recent years, awareness or consciousness of people about an antibacterial action and a deodorizing action becomes high and as a result, many proposals have been made for them. For example, a method of utilizing a photo-catalyst is known.

[0003]

For example, a sterilizing reactor is disclosed in Japanese Patent Publication No. Hei 5-50294 (1993), in which fine particles of photo semiconductor are fixed on the surface of a base member to provide a photo-sterilizing filler. In this manner, it is possible to attain sterilization more than 99% in three (3) hours.

[0004]

However, in such a reactor, a mixture of high polymer material and dust adheres onto the surface of the semiconductor that is a catalyst for causing photo-catalytic reaction and covers the surface thereof. Accordingly, ultraviolet rays cannot reach the catalyst and it is difficult for the catalyst to receive energy. As a result, the photo-catalytic reaction is lowered to cause deterioration in reaction. On the other hand, disclosed in Japanese Patent Publication No. Hei 6-7905 (1994) is a deodorizing apparatus using a photo-catalyst, which comprises a photo-catalyst layer consisting of a semiconductor, an ultraviolet (UV) ray lamp and a heat generating body which are provided in opposition to the photo-catalyst layer, and a ventilator, wherein the photo-catalyst layer or the heat generation body, or both the photo-catalyst layer and the heat generating body move(s) so that the entire photo-catalyst layer is heated in sequence. However, the deodorizing apparatus becomes complicated because a means for regenerating activity of the photo-catalyst layer is needed.

[0005]

Also, in particular, in the case where material forming the photo-catalyst layer

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is made of titanium oxide, phase transition is caused at a temperature higher than 900 °C from an anatase-type showing high photo-catalytic activity to a rutile-type showing low photo-catalytic activity. Accordingly, when trying to bond between the particles of titanium oxide by a neck portion formed by the solid-phase sintering by means of only a heat treatment, the phase transition to the rutile-type is caused to lower the photo-catalytic activity, unless the particles of titanium oxide are sintered at a low temperature by making considerably fine particles of titanium oxide the starting material.

[0006]

[Problem to be Solved by the Invention]

To solve these two problems at the same time, there is a method for covering active spots of fine particles having photo-catalytic activity with metal fine particles of Ag, Cu, Pt, Pd, Au, Ni, Fe, Co, Zn, or the like. However, since these metals belong to the colored metals, the surface of the base member is colored with the peculiar or inherent color thereof when applied too much and as a result, a color of the base member or a design such as the patterns is deteriorated.

[0007]

[Means for Solving the Problem]

To solve the above-mentioned problems according to the present invention, there is provided a method for manufacturing a member provided with catalysts including metal fine particles, comprising the steps of fixing particles having photo-catalytic activity and colored metal fine particles on a base member and forming achromatized or whitened salt on at least surfaces of the metal fine particles through reaction between said metal fine particles and an aqueous solution or a gas. It is therefore an object of the present invention to provide a decolorizing method that does not deteriorate a color of the base member and a design such as the patterns, while keeping high photo-catalytic activity.

[0008]

The particles having photo-catalytic activity are semiconductor particles having a sufficient band gap to perform photo-catalytic functions including an antibacterial function, a deodorizing function, or the like. According to one theory, the photo-catalytic particles also have antibacterial properties because bacteria are electrocuted by application of a voltage higher than a predetermined level. However, it is generally considered that the particles have the antibacterial properties due to active oxygen produced at the time of light irradiation as seen in the deodorizing function. For producing active oxygen, it is necessary that a conduction band of the semiconductor as represented by a band model be positioned higher than a hydrogen generating potential,

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and that an upper end of a valence band be positioned lower than an oxygen generating potential. The semiconductor that can satisfy such requirements includes  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{ZnO}$ ,  $\text{SiC}$ ,  $\text{GaP}$ ,  $\text{CdS}$ ,  $\text{CdSe}$ ,  $\text{MoS}_3$ , or the like. Since the position of the conduction band moves upwardly in the case of fine particles, there is some possibility that fine particles of  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ , or the like having a diameter of a range from 1 to 10 nm also generate the active oxygen. Anatase-type  $\text{TiO}_2$  is particularly preferable among these materials because it can obtain highly active and chemically stable fine particles at a low cost.

[0009]

The colored metal fine particles mean fine particles of metals such as Ag, Cu, Pt, Pd, Au, Ni, Fe, Co, or Zn which have a low ionization tendency and is easily reduced by itself. In case of forming achromatized or whitened salt through an aqueous solution reaction, or in case of using a catalyst including metal fine particles within a liquid, it is desirable that the formed achromatized or whitened salt be hard to solve or insoluble. Further, herein the achromatization or whitening means decolorizing to the extent less than 2 in the color-difference with respect to a ground, but it is not always necessary to be achromic (colorless) or pure white.

[0010]

Herein, the order or sequence in conducting the two steps mentioned above may be changed, therefore it does not matter to start any one of them first. Thus, the catalyst containing metal fine particles may be manufactured after fixing the particles having photo-catalytic activity on a base member in advance, or alternately the particles having photo-catalytic activity may be fixed on the base member after manufacturing the catalyst containing metal fine particles.

[0011]

The base member may be basically made of ceramic, ceramic material, metal, glass, a thermosetting resin, a thermoplastic resin, or a composite thereof. Further, the base member may basically have any shape, for example, a simple shape like a plate or sheet-like material such as a tile, a wall material or a floor material, and a rod-like material, a ball-like material, a column-like material, a cylindrical material, a prismatic material, or a hollow prismatic material, or may have a complex shape such as sanitary ware, a washstand, a bathtub, a sink, or accessories thereof.

[0012]

A first embodiment in which the catalyst including metal fine particles is manufactured after fixing the particles having photo-catalytic activity on a base member

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in advance comprises the steps of forming a layer of particles having photo-catalytic activity on a base member, fixing colored metal fine particles on the layer of particles and forming achromatized (colorless) or whitened salt to cover said colored metal fine particles, wherein those steps are carried out in this order.

[0013]

Basically, the step for forming the layer of particles having photo-catalytic activity on the base member is conducted through a heat treatment, after applying a starting material or a material to which an appropriate treatment is added upon the surface of the base member. The starting material includes a sol of a material having photo-catalytic activity, an alkoxide containing a metallic element constituting the material having photo-catalytic activity, an organic metal salt, an inorganic acid salt, halogenated salt, or the like. For example, in a case of using a sol of anatase-type titanium oxide as the starting material, an isoelectric point of the titanium oxide is PH6.5 which is nearly neutral. Accordingly, it can be uniformly applied on a surface of the base member by using a suspension dispersed by an acid or an alkali.

[0014]

In such dispersion treatment, when the base member is made of a metal, alkali dispersion is desirable from a viewpoint of corrosion resistance. In the case of a pottery, a tile, ceramics, etc., any one of an acid or alkali dispersion fluid may be used. An acid to be used in this case can be nitric acid, sulfuric acid, hydrochloric acid, acetic acid, phosphoric acid, organic acid, etc. In the case of an alkali, ammonia, or hydroxides including alkaline metals and alkaline earth metals can be used. However, in ammonia is particularly preferable among them because it generates no metal contamination after heat treatment. It is also possible to add a dispersing agent of an organic or phosphoric acid group, a surface-active agent, a finishing agent, or the like into such dispersion fluid.

[0015]

Also, in the case of using a sol as the starting material, it is preferable that an average diameter of the sol of the material having photo-catalytic activity be  $0.05\mu\text{m}$  or less, if possible be  $0.01\mu\text{m}$  or less because the smaller the average diameter, the higher the photo-catalytic activity. Herein, the average diameter can be obtained by the Scherrer equation from an integrated width of the maximum peak of a crystal when conducting the powder X-ray diffraction analysis of the sol.

[0016]

When the sol is used as the starting material, there are methods for coating the suspension fluid of the sol onto the surface of the base member by spray coating, roll

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coating, dip coating, spin coating, CVD, electron beam evaporation, or sputtering. One of these methods may be used or a method other than these can also be used. However, the spray coating method, the roll coating method, and the dip coating method have advantages that no special equipment is required for coating at a low cost compared with the CVD method, the electron beam evaporation method, the sputtering method or the like.

[0017]

When the alkoxide is used as the starting material, a mixed liquid applied, which is obtained by adding an appropriate diluent and if necessary, a hydrolysis depressant such as hydrochloric acid to the alkoxide. Herein, the appropriate diluent preferably includes alcohol such as ethanol, propanol and methanol, but it should not be limited to those. However, water should not be contained therein as far as possible. If containing water therein, hydrolysis is explosively accelerated in many alkoxides such as titanium alkoxide and it results in a reason of generating cracks therein. The alkoxide is applied onto the base member, for example, by a flow coating method whereby a dry air is used as a carrier.

[0018]

When the alkoxide, an organic metal salt, an inorganic acid salt, halogenated salt, and the like are used as the starting material, the heat treatment after application is carried out at the same time when these precursors are changed into oxides and crystallized and at the temperature in which the particles having photo-catalytic activity obtained in this manner are immobilized onto the surface of base member with high bonding strength. The temperature is, for example, between 400°C and 800°C when the particles having photo-catalytic activity is anatase-type titanium oxide.

[0019]

On the contrary, when the sol is used as the starting material, since it already contains crystals of oxide therein, the heat treatment can be made at a temperature whereby the particles having photo-catalytic activity are immobilized onto the surface of base member with high bonding strength. However, the bonding strength of the sol to the base member is relatively weak compared with the precursors unless the sol is of considerably fine particle. Accordingly, when the particles having photo-catalytic activity is, for example, titanium oxide, the heat treatment must be conducted at a temperature higher than 800°C unless a special means such as viscosity blending is used.

[0020]

In the step for forming a layer of particles having photo-catalytic activity on

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the base member, a binder layer may be interposed between the base member and the layer of particles having photo-catalytic activity to be formed. As a result of this, it is possible to further strengthen the bonding between the layer of particles having photo-catalytic activity and the base member.

**[0021]**

As such a binder, either of a thermoplastic binder such as glaze, inorganic hyaline, a thermoplastic resin or soft solder may be used or a thermosetting binder such as a thermosetting resin or a photo-setting resin may be used.

**[0022]**

In the case of using a thermoplastic binder, a particle layer having photo-catalytic activity is formed on the base member by conducting, in order, the steps for forming a binder layer on the surface of the base member, forming a layer having photo-catalytic activity on the binder layer, and conducting heat treatment at such a temperature that the upper most surface of the layer having photo-catalytic activity is exposed and the lower layer thereof is partly embedded in the binder layer.

**[0023]**

Herein, the step for forming the binder layer on the surface of the base member is conducted by applying a binder component of which the softening temperature is lower than that of the base member on the base member. The binder component does not necessarily agree with composition of the binder layer when a member is completed. For example, when the binder is of inorganic hyalin (glassy material), a material to be applied to may be suspended liquid of inorganic hyalin composition such as a granular-shape, a frit-shape, a block-shape or powder, or may be mixed liquid of salts containing the constituent metal composition. There are methods of application such as a spray coating method, a roll coating method, and a dip coating method and either method can be used.

**[0024]**

Before conducting the step for forming the layer of particles having the photo-catalytic activity on the binder layer, the binder layer applied may be dried up to evaporate water, etc. contained therein. As a drying method in this instance, there is known a method for leaving the binder layer at room temperature or a method for heating the binder layer together with the base member. Further, before conducting the step for forming the layer of particles having the photo-catalytic activity on the binder layer, the binder layer applied may be heat-treated at a temperature lower than a softening temperature of the base member whereby the binder layer changes and softens in the composition of the binder layer when the member is completed. According to



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this method, the binder layer is flattened further in advance when the layer of particles having the photo-catalytic activity is formed on the binder layer. Accordingly, an effect can be fully exhibited even if the particles having the photo-catalytic activity to be applied are small in an amount thereof.

[0025]

The step for forming the layer of particles having the photo-catalytic activity on the binder layer is basically the same as that for directly forming the layer of particles having the photo-catalytic activity on the base member. A step for conducting the heat-treatment at such a temperature that the upper-most surface of the layer having photo-catalytic activity is exposed and the lower layer thereof is partly embedded in the binder layer is performed at a temperature lower than the softening point of the base member whereby the binder layer changes and softens relative to the composition of the binder layer when the member is completed. It is generally desirable that the heat treatment be made at a temperature higher than the softening temperature of the binder layer by 20 - 320°C. In this manner, the particles having the photo-catalytic activity moves into the binder layer appropriately, wherein the upper-most surface of the layer having photo-catalytic activity is exposed and the lower layer thereof is partly embedded into the binder layer. Also, when a thermosetting binder is used, for example, the steps for mixing the binder with a curing agent to be applied onto the base member, increasing viscosity of the mixture, applying particles having the photo-catalytic activity, and curing the binder by the heat treatment are performed in order to form the layer of particles having photo-catalytic activity on the base member.

[0026]

The method for mixing the binder with the curing agent to be applied on the base member is conducted, for example, by applying mixed liquid obtained by adding a diluent first to a thermosetting resin and then adding a curing agent thereto to the surface of the base member. Herein, the diluent is applied to lower the viscosity of the mixed liquid, thereby enabling easy application of the mixed liquid on the surface of the base member. Accordingly, the diluent used herein may be basically any solvent as far as it achieves such an object. For example, water, ethanol, propanol, etc. can be used as the diluent.

[0027]

As a method for applying the mixed liquid on the base member, there are already known a spray coating method, a roll coating method, a dip coating method, the spin coating method, etc. Any one of these methods or any other method may be used.

[0028]

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In a step for increasing the viscosity of the mixture, the viscosity increase of the mixture is effected by heat treatment or by leaving the mixture as it is. It is preferable that the increased viscosity be between  $10^5$  poise and  $10^{7.5}$  poise. The particles having photo-catalytic activity are applied after the mixture has a high viscosity value of  $10^5$  poise or more because this enables the photo-catalytic particles to be embedded in the binder layer in such a condition that the photo-catalytic particles are not embedded completely therein. On the other hand, when the increased viscosity is  $10^{7.5}$  poise or less, at least the lowermost part of the layer of particles having photo-catalytic activity can be partly embedded in the upper layer of the binder.

[0029]

A step for immobilizing colored metal fine particles on the layer of particles having photo-catalytic activity is performed by applying a solution containing at least one kind of colored metals such as Ag, Cu, Pt, Pd, Au, Ni, Fe, Co and Zn to the layer and by irradiating light including UV light on the surface to applied.

[0030]

Herein, as such a solution containing the colored metal therein, a solution of soluble salt of the above-mentioned metals is desirable. For example, the following solutions and/or the mixed solutions thereof can be used: silver nitrate, silver sulfate, silver acetate, silver fluoride, silver chlorate, copper (I) acetate, copper (II) acetate, copper (II) chlorate, copper (II) chloride, copper (I) sulfate, copper (II) sulfate, copper (II) bromide, copper (II) nitrate, ferrous chloride, ferric chloride, ferrous sulfate, ferric sulfate, ferrous iodide, ferric bromide, ferrous bromide, ferric oxalate, ferrous acetate, ferric acetate, ferric chlorate, ferrous chlorate, ferric nitrate, ferrous nitrate, cobalt chloride, cobalt sulfate, cobalt iodide, cobalt bromide, cobalt acetate, cobalt chlorate, cobalt nitrate, nickel chloride, nickel sulfate, nickel iodide, nickel bromide, nickel acetate, nickel chlorate, nickel nitrate, palladium sulfate, palladium chloride, platinum chloride, platinum sulfate, auric chloride, auric sulfate, auric bromide, zinc chloride, zinc sulfate, zinc iodide, zinc bromide, zinc acetate, zinc chlorate, zinc nitrate, etc. As a method for applying the solution, any method is basically acceptable, but the spray coating method is simple and easy. The spray coating method is also desirable and advantageous in that the coating can be done with a small amount of solution to be used, that the solution can be applied equally, the film thickness can be controlled easily, and that the solution can be applied onto only a front surface if no coating is needed on the reversed surface thereof.

[0031]

When applying the solution by means of the spray coating method, it is

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preferable to dry up coatings before irradiating the light rays including the UV light upon it. This is because an immobilization ratio of metal can be improved with respect to an amount of coating and it is advantageous from a viewpoint of costs. Also, a solvent when applied by the spray coating method should not be limited basically and various solvents such as water, ethanol, propanol, or methanol can be used. If the dispersibility among them is same, it is most preferable to use ethanol. Since ethanol is faster in drying rate than water or the like, the time necessary for the drying step can be shortened, thereby improving productivity. Also, since the surface tension of ethanol is low, it shows superior wettability into the layer of particles having the photocatalytic activity. Further, it is less toxic compared with the other volatile solvents such as methanol or the like, thus it is harmless. When water is used for the reason of dispersibility, etc., it is preferable to add a small amount of sacrificial oxidizing agent such as alcohols, unsaturated hydrocarbon because it accelerates photo-reduction reaction.

[0032]

A light source for irradiating the light rays including the UV light may be, for example, a ultraviolet lamp, a RLB lamp, a xenon lamp, a mercury vapor lamp, a fluorescent tube, or the like which can irradiate the UV light therefrom. When irradiating the light rays including the UV light, it is preferable that a sample be disposed to allow the light to be incident upon the irradiation surface at the right angle (90°). In this manner, it is most efficient to irradiate the light

[0033]

A step for forming the achromatized (colorless) or whitened salt to cover the colored metal fine particles is conducted by, for example, a method for bringing the metal fine particles in contact with a solution which is able to form the achromatized or whitened salt on at least the surfaces of the metal fine particles by reacting upon the colored metal fine particles, or by a method for bringing the metal fine particles in contact with a reaction gas which is able to form the achromatized or whitened salt on at least the surfaces of the metal fine particles by reacting upon the colored metal fine particles.

[0034]

It is preferable that substance achromatized or whitened by the salt of the colored metal fine particles mentioned above be a salt that is hard to solve or insoluble. This is because the salt can be formed easily on at least the surface of the metal fine particles through an aqueous solution reaction, and it can be used with stability under the circumstance containing water.

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[0035]

Substance whitened or achromatized by the salt of the colored metal fine particles mentioned above includes, for example, silver chloride, silver bromide, silver iodide, silver oxalate, silver thiosulfate, silver cyanide, silver rhodanide, copper (I) chloride, copper (I) bromide, copper (I) cyanide, copper (I) rhodanide, cuprous oxide, zinc phosphate, zinc oxalate, zinc cyanide, palladium cyanide, zinc sulfide, zinc carbonate, ferric carbonate, zinc oxide, etc. A solution which is able to form the salts mentioned above include, for example, in the case of silver chloride, potassium chloride solution, sodium chloride solution, ammonium chloride solution, ferric chloride solution, and the like, and in the case of silver iodide, it includes potassium iodide solution, sodium iodide solution, ferric iodide solution, etc. However, the solution should not be limited only to them, but various soluble salt solutions containing each negative ions of salt can be used widely. Further, if various kinds of salts above are oxides such as zinc oxide or cuprous oxide, oxidant water such as hydrogen peroxide water or ozone water can also be used.

[0036]

Also, reaction gas which can form the salt above can also be widely used if the gas is a gaseous body containing negative ion element of each salt. For example, if the salt is an oxide such as zinc oxide or cuprous oxide, it is possible to form a layer of oxide on the surface through oxidization of the surfaces of the metal fine particles by heating them in the air, oxygen or water vapor, etc., or by causing them to react with the oxidizing agent such as ozone, etc.

[0037]

Also, the layer of particles of which the base member is provided with photo-catalytic activity may be formed with a mixed layer of particles having photo-catalytic activity and resin. Even in such a structure, it is possible to make the bonding between the layer of particles having photo-catalytic activity and the base member stronger. In this case, it is not necessary to allow the particles having photo-catalytic activity to be exposed to contact with an external air. Accordingly, when applied on the base member, it is not necessary to carry out the step for applying the particles having photo-catalytic activity and the step for applying the binder separately. It is therefore possible to mix the particles having photo-catalytic activity with the binder so that application can be performed only one time. Thus, simplification of the steps can be achieved, thereby obtaining reduction in the manufacturing costs.

[0038]

Herein, if the resin is not the material for absorbing the UV light extremely, but

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it has corrosion-resistance against the light in a certain degree, it does not matter if the resin has the thermoplastic property, thermosetting property or photo-setting property. In this case, many particles having photo-catalytic activity are embedded in the resin. Accordingly, it is concerned that no photo-catalytic activity is caused, but, in fact, the metal fine particles such as silver, copper, platinum, palladium, gold, nickel, iron, cobalt or zinc can be carried. As a result, the photo-catalytic activity is not lost. The mechanism will now be outlines below.

[0039]

It is understood that the photo-catalytic reaction proceeds on the particles having photo-catalytic activity as follows. First, a reaction whereby a photon is decomposed into an electron and a positive hole is caused. Namely:



Next, the positive hole generated reacts on oxygen or water in the air or the layer and generates an active oxygen type. The chemical reaction formula when reacted on water is expressed by the following (2) and (3).



The active oxygen type  $OH \cdot$  generated herein acts on odor elements and/or bacteria and exhibits deodorizing properties and/or antibacterial properties. However, the reaction of the formula (3) competes with a reaction expressed by the formula (4), where the positive hole and the electron rejoin and return to the photon.



[0040]

First of all, consideration will be made on a case where the particles having photo-catalytic activity are exposed. In this case, oxygen or water in the air or the layer can contact the particles having photo-catalytic activity directly. Accordingly, when the decomposing reaction of light expressed by the formula (1) takes place, oxygen or water as well as the positive hole and electron exist on the particles having photo-catalytic activity. In this instance, the formulae (3) and (4) are in competition. Therefore, the active oxygen is generated at a certain probability according to the formula (3) (probability of about 20% in the case of anatase-type titanium oxide). With the action of this active oxygen, the photo-catalytic reaction such as the deodorizing action and/or antibacterial action is caused. Next, consideration will be made on a case where the particles having photo-catalytic activity are completely covered with the binder in such a condition that no metal mentioned above lies in the periphery. Since being covered with the binder, oxygen or water cannot contact the

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photo catalysts directly. Accordingly, to realize reaction of oxygen or water and the positive hole according to the formula (3), it is necessary for oxygen or water to disperse on particles having the photo-catalytic activity, or for the positive hole to disperse on the upper most surface where oxygen or water lies, or for both of the dispersion above to occur. An induction period is caused for this. On the other hand, electrons already exist on the particles having photo-catalytic activity when the decomposition reaction of the photon is caused. For this reason, before causing the dispersion above, i.e. during the period of induction, the reaction according to the formula (4) is generated and as a result, active oxygen generating reaction according to the formula (3) is hardly caused.

[0041]

From the above, in the case where the particles having photo-catalytic activity are mostly covered with the binder in such a condition that no such a metal above lies in the periphery thereof, the active oxygen is generated at a certain probability only on the portion where the particles having photo-catalytic activity are exposed. For this reason, an amount of the active oxygen generated is small and as a result, the photo catalytic functions such as deodorizing action and/or antibacterial action cannot be fully exhibited.

[0042]

On the other hand, when the metal fine particles lie in the vicinity of the particles having photo-catalytic activity (i.e. in a condition that the metal fine particles do not necessarily come in contact with the particles having photo-catalytic activity), even if the particles having photo-catalytic activity are completely covered with the binder, the electrons produced according to the formula (1) are caught by these metal fine particles. Accordingly, the recombination reaction according to the formula (4) is hard to occur and the positive holes can reside or stay for a long time without disappearance. Accordingly, even if the particles having photo-catalytic activity are covered with the binder so that the active oxygen generating reaction according to the formula (3) exhibits the induction period due to the reasons above, the positive holes are difficult to disappear according to the formula (4). Thus, the active oxygen generating reaction according to the formula (3) occurs during the induction period.

[0043]

According to the above-mentioned mechanism, if at least one (1) kind of metal fine particles such as silver, copper, platinum, palladium, gold, nickel, iron, cobalt or zinc is included, the photo-catalytic functions such as the deodorizing action and/or antibacterial action can be exhibited, even if the particle having the photo-catalytic

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activity are mostly covered with the resin.

[0044]

One embodiment of a method for forming the layer of particles having photo-catalytic activity in this case comprises, for example, a step for adding thermosetting resin to a suspension obtained by dispersing sol of substance having photo-catalytic activity, a step for diluting the suspension of mixture between the sol and a resin by a solvent, a step for further adding a hardening agent to the diluted liquid, a step for applying the liquefied material added with the hardening agent onto a base member, and a step for heat-treating the base member to which the liquefied material has been applied, wherein these steps are performed in order. And, in this case, a step for immobilizing the colored metal fine particles onto the particles having photo-catalytic activity and a step for forming the achromatized (colorless) or whitened salt on at least the surfaces of the metal fine particles by causing a solution or a gas to react on the metal fine particles are conducted in the same manner as described above.

[0045]

Herein, the step for causing the colored metal fine particles to react on the solution or gas to form the achromatized (colorless) or whitened salt on the surfaces of the metal fine particles may be performed after the fine particles are carried or held on the surface of particles having photo-catalytic activity before mixing with the resin. Also, after forming the achromatized (colorless) or whitened salt on the surface of metal fine particles, the metal fine particles and the particles having photo-catalytic activity may be mixed together with the resin, thereby forming a member having catalysts containing the metal fine particles on the base member in the same manner as described above.

[0046]

Herein, the diluent which is used in the step for diluting the suspension of mixture between the sol and the resin by solvent is added for the purpose of lowering the viscosity thereof and for providing easy application to the base member. Any diluent can be basically used as far as it achieves the object above and it includes, for example, ethanol, propanol, water, etc. A drying step may be inserted between the step for applying the liquefied material added with the hardening agent onto the base member and the step for heat-treating the base member on which the liquefied material is applied. Any method can be used for applying the liquefied material added with the hardening agent onto the base member, but the spray coating method or the roll coating method is relatively simple and easy.

[0047]

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The heat treatment may be conducted at a low temperature of 100°C or less for a long time or it may be conducted at a high temperature of 100°C or more and below the heat-resistant temperatures of the base member and the thermosetting resin for a short time. In general, the particles having photo-catalytic activity have larger specific gravity than the thermosetting resin. Accordingly, it is desirable that the heat-treatment be conducted at a temperature of 100°C or more and below the heat-resistant temperature of the base member and the thermosetting resin for a short time, because there is no worry that the particles having photo-catalytic activity are embedded in the lower layer section of the surface of the base member. Another embodiment of a method for forming a layer of particles having photo-catalytic activity in the case where a layer of particles having photo-catalytic activity is formed by a mixture layer between the particles having photo-catalytic activity and a resin comprises, for example, the steps of: mixing a solution containing at least one kind of metals such as silver, copper, platinum, palladium, gold, nickel, iron, cobalt or zinc with a suspension in which the sol of substance having photo-catalytic activity is dispersed; irradiating light rays including the UV light upon the mixed liquid to immobilize the metal to the sol of substance having photo-catalytic activity; causing the metal fine particles to react on a solution or a gas to form achromatized (colorless) or whitened salts on at least the surfaces of the metal fine particles; adding a thermosetting resin onto said mixed liquid; diluting the suspension of mixture between said sol and the resin by a solvent; adding a hardening agent further to said diluted liquid; applying added liquefied material onto a base member; and heat-treating the base member onto which the liquefied material has been applied; wherein the above steps are performed in order. In this case, the catalytic particles containing the metal fine particles are formed in advance before immobilizing on the base member.

[0048]

Herein, in the method for mixing the solution containing at least one kind of metal of Ag, Cu, Pt, Pd, Au, Ni, Fe, Co, Zn, or the like with the suspension in which sol of substance having photo-catalytic activity is dispersed, it is desirable that a metalline solution adjusted to have almost the same pH as the suspension is added to the suspension in which the sol of substance having photo-catalytic activity is dispersed. This is because the dispersibility of sol of substance having photo-catalytic activity can be maintained by making the zeta potential of the sol of substance having photo-catalytic activity in the liquid unchanged so much.

[0049]

In a step for immobilizing the metal to the sol of substance having the photo-



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catalytic activity by irradiating the light rays including the UV light on the mixed liquid, it is desirable that the step be performed while stirring the mixed liquid. This is because it is easy for the stirring to make the metal uniformly adhering to the sol of substance having the photo-catalytic activity. For example, an ultrasonic vibrator, a stirrer, a homogenizer, etc can be used as a stirring apparatus in this case.

[0050]

In a method for irradiating the light rays including the UV light, any method is basically acceptable, but it is preferable to irradiate from an upper portion of a container, because no absorption of the UV light by the container occurs. In a method for forming two (2) particle layers having photo-catalytic activity in the case where a layer of particles having photo-catalytic activity on the base member is formed by a mixed layer between the particles having photo-catalytic activity and the resin, it is also possible to apply the thermosetting resin to the base member in advance. In this manner, if the thermosetting resin is inserted between the base member and the mixed layer of the particles having photo-catalytic activity and the resin, the following effects can be obtained.

[0051]

First, it is possible to firmly bond the base member with the mixed layer of the particles having photo-catalytic activity and the resin, thereby improving peeling resistance. This is because a film made of only the thermosetting resin is higher in the film strength than the mixture between the thermosetting resin and the particles having photo-catalytic activity of an inorganic crystalline and it is superior in adhesion properties.

[0052]

Second, it is possible to improve the film strength by putting the thermosetting resin layer therebetween, thereby lowering an amount of the thermosetting resin within the mixed layer between the particles having photo-catalytic activity and the resin on the surface of the base member. With this, it is possible to concentrate the distribution of the particles having photo-catalytic activity in the vicinity of the uppermost surface and as a result, the photo-catalytic activity can be easily exhibited and the photo-catalytic functions such as the antibacterial action and/or the deodorizing action, etc. improve.

[0053]

Third, the resin to be inserted herein is not always necessary to be the same kind as the resin within the mixed layer between the particles having photo-catalytic

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activity and the resin. For example, it is preferable for the resin within the mixed layer between the particles having photo-catalytic activity and the resin to have a certain degree of photo-corrosion resistance. However, as it is not necessary for the resin to be inserted herein, the resin may be made of an inexpensive resin or a colored resin. Also, in the case where the difference in thermal expansion between the base member and the particles having photo-catalytic activity is remarkably large, it is possible to solve the possibility of producing cracks etc. during heat treatment if the resin to be inserted is formed by an elastic resin or a resin having an intermediate thermal expansion coefficient.

[0054]

It is desirable that an amount of the resin within the mixed layer between the particles having photo-catalytic activity and the resin in this case be between 5 % by weight and 50 % by weight. This is because when the amount of resin is 5 % by weight or less, abrasive resistance on the surface of the base member is not sufficient. On the other hand, when the amount of resin is 50 % by weight or more, an absolute amount of the particles having photo-catalytic activity is insufficient and as a result, sufficient deodorizing and antibacterial function can not be obtained.

[0055]

The method for applying the thermosetting resin onto the base member in advance comprises the steps of dispersing the thermosetting resin into the solvent, adding a hardening agent into the dispersion liquid mentioned above, applying the liquefied material added with the hardening agent onto the base member, drying up the liquefied material applied on the base member, wherein these steps are performed in order.

[0056]

[Functions]

By covering the active points of the particles having photo-catalytic activity with the colored metal such as silver, copper, platinum, palladium, gold, iron, nickel, cobalt or zinc, it is possible to prevent the photo-catalytic activity from being lowered by adhesion of giant molecules and/or dusts thereon. Also, high temperature treatment or the like is performed to firmly immobilize the particles having photo-catalytic activity on the base member. In this manner, it is possible to recover the photo-catalytic activity by covering the photo-catalytic activity that has dropped with the colored metal. Further, according to the method for causing at least the surfaces of the metal fine particles to react on a solution or a gas so as to form the achromatized (colorless) or whitened salt, it is possible to decolorize without deteriorating a design of the base

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member such as the color or patterns.

[0057]

[Embodiments]

(Embodiment 1)

A sol of titanium oxide of which the average particle size is  $0.01\mu\text{m}$  is first applied onto the surface of a tile base member of 15 cm square and then heat-treated at  $900^\circ\text{C}$ , thereby forming a thin film of rutile-type titanium oxide. A sample stopped at this stage is referred to as "comparative sample 1". After this, an aqueous solution of silver nitrate is applied according to the spray coating method and light from a light source of BLB lamp of 20W is irradiated for ten (10) minutes thereupon, whereby silver is immobilized on a thin film of rutile-type titanium oxide. In this case, an amount of silver carried or held therein is  $1.2\mu\text{g}/\text{cm}^2$ , and it shows brown color. A sample stopped at this stage is referred to as "comparative sample 2". Thereafter, a solution of potassium iodide of 0.1 mol/liter is applied on a comparative sample 2 at a ratio of  $0.1\text{cc}/\text{cm}^2$  for reaction. As a result of this, the surface of the sample changes to a yellow-white color and was whitened. It is considered that a layer of silver iodide has been formed. This sample is referred to as "exemplary sample 1".

[0058]

With these samples, evaluation was made on a color difference, photo-activity, a deodorizing properties, and antibacterial properties. Measurement of the color difference was made by means of a spectral color difference meter (made by Tokyo Denshoku, Ltd.). In this case, a standard sample is made as a "comparative sample 1". The result is shown in Fig. 1. As a result, the color difference was 3.5 in the comparative sample 2. On the contrary, the color difference decreased to 1 in the exemplary sample 1 and the degree of color also decreased due to the fact that it has been treated by the aqueous solution of potassium iodide.

[0059]

The photo-activity was evaluation through a  $\Delta\text{PH}$  testing. The  $\Delta\text{PH}$  testing is a method whereby the aqueous solution of potassium iodide is dropped on the surface of the sample, and then UV light is irradiated upon the dropped aqueous solution of potassium iodide for thirty (30) minutes, thereby evaluating the photo-activity from the difference between PH of the aqueous solution of potassium iodide before and after irradiation. Thus, according to this method, if the photo-activity is high on the surface of sample, since such oxidation-reduction reaction as indicated below proceeds further, the PH after irradiation becomes higher than the PH before irradiation.

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Oxidation reaction:  $Zn + 2h^+ = Zn^{2+}$ Reduction reaction:  $O_2 + 2H_2O + 4e^- = 4OH^-$ 

[0060]

Also, the deodorizing properties were evaluated by R30 (L). The R30 (L) means a ratio of odor rejection after light irradiation. Specifically, the R30 (L) can be obtained by: putting a sample into a glass vessel of 11L; disposing the surface of sample on which the thin film is formed, at a distance of 8 cm from a light source (i.e. the BLB fluorescent lamp of 4W); injecting a methyl mercaptan gas into the vessel so that the gas has the initial concentration of 3 ppm, and then measuring the change in concentration when light has been irradiated thereon for thirty (30) minutes.

[0061]

Results of the photo-activity and the deodorizing properties are shown in Fig. 2. Comparison between the comparative samples 1 and 2 shows that the comparative sample 2 restores or recover the photo-activity by carrying silver thereon, and it also shows good results both in the  $\Delta PH$  and in the R30 (L). Also, when comparing the exemplary sample 1 with the comparative sample 2, both the  $\Delta PH$  and the R30 (L) had almost the same values. Under these circumstances, it was known that the photo-activity is not affected by the decolorizing treatment and good characteristics or properties can be maintained.

[0062]

Also, the antibacterial properties were tested using *Escherichia coli* (*Escherichia coli* W3110 stock). An amount of 0.15 ml ( $2 \times 10^4$  CFU) of a bacteria liquid was dripped on the uppermost surface of the sample which has been disinfected in advance by 70% of ethanol. It was then put on a glass plate (100×100) to allow the bacteria liquid to contact with the uppermost surface of the base member, thereby making samples. A sample (L) was irradiated by a white lamp (3,500 lux) for a predetermined time, while a sample (D) was kept under glare protection. Each bacteria liquid on the samples (L) and (D) was wiped with sterilized gauze to collect them into physiological saline and then, the number of the live bacteria therein was examined for evaluation.

[0063]

A result relating to the antibacterial properties is shown in Fig. 3. Since no silver is carried on the comparative sample 1, antibacterial effect cannot be acknowledged when it is dark (D). On the contrary, in the case of the exemplary example 1, the antibacterial effect could be acknowledged when it is dark (D), although the surface of silver has changed into chemical compound through the decolorizing

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treatment. When the sample was irradiated (L), the antibacterial effect can be observed more strongly, wherein not only the antibacterial effect of silver, but also a recovery effect of the photo-catalytic activity of a rutile-type titanium oxide thin film could be observed.

[0064]

(Embodiment 2)

After mixing fluorine contained resin with anatase-type titanium oxide as a binder and applying the mixture onto an acrylic resin plate with a thickness of 100  $\mu\text{m}$ , the mixture is dried up for adhesion. After applying an aqueous solution of silver nitride of 0.001 wt.% - 0.1 wt.% on the adhesion, UV light is irradiated thereupon, so as to deposit silver on the film of titanium oxide, and further an aqueous solution of potassium iodide of 0.1 mol/liter is applied on the surface of silver at a ratio of 0.1 cc/ $\text{cm}^2$ . When irradiating the UV light thereupon, the decolorization occurs, and the color difference goes down from 4 to 1.2 (4  $\rightarrow$  1.2). Also, the deodorizing properties R30 (L) were about 90% and the result was satisfactory.

[0065]

(Embodiment 3)

Upon injection molding of a plastic product, a mixture of powder of anatase-type titanium oxide and silver powder is applied in advance on a surface of an injection die. And, after forming a layer made of titanium oxide and silver on a surface of the plastic by an injection molding, it is dipped into an aqueous solution of potassium iodide of 0.1 mol/liter. When irradiating the UV light thereupon, the decolorization occurs, and the color difference went down from 3 to 0.8 (3  $\rightarrow$  0.8). Also, the deodorizing properties R30 (L) are about 80% and the result was satisfactory.

[0066]

(Embodiment 4)

After applying glaze onto a base for forming a sanitary ware of 15 cm square and baking the base at a temperature between 1,100 and 1,200  $^{\circ}\text{C}$ , a sol of an anatase-type titanium oxide of which the average particle size is 0.01  $\mu\text{m}$  is applied to the base and baked at a temperature between 900 and 1,000  $^{\circ}\text{C}$ , thereby immobilizing a thin film of a rutile-type titanium oxide on the base material for the sanitary ware. After this, by applying an aqueous solution of silver nitride onto the base and irradiating UV light, silver was caused to deposit on the thin film of titanium oxide. Further, when an aqueous solution of ferric chloride is applied onto the thin film and the UV light is irradiated thereupon, the thin film is decolorized, wherein the color difference went down from 3 to 0.3 (3  $\rightarrow$  0.3). Also, with reference to the antibacterial properties, by

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bringing the bacteria in contact with the sample for thirty (30) minutes both when lights are irradiated and when it is dark, it was confirmed that only the bacteria of 10% or less of the original number of bacteria are live. Thus, the antibacterial properties showed a satisfactory result.

[0067]

(Embodiment 5)

After mixing nitric acid dispersed liquid of an anatase-type titanium oxide sol of which the average particle size is  $0.01\ \mu\text{m}$  and a siloxane clear coat resin having a water repellent property at a predetermined weight ratio and diluting the mixture by propanol, a solution added with a hardening agent was applied to an alumina base. After application, the base was baked at a temperature of  $150\ ^\circ\text{C}$  so as to solidify and then it was cooled. In addition, a copper acetate aqueous solution was applied to the base. After this, a sample was obtained by conducting a photo-reduction (the light source: 20-watt BLB lamp, the distance from the light source to the sample: 10 cm, and the irradiation time: 15 min.). The film thickness of the mixed layer obtained in this manner is about  $0.8\ \mu\text{m}$  and the crystal was an anatase-type. Further, when conducting this photo-reduction treatment in the air, copper is immobilized in a decolorized condition. This is considered that since copper immobilized by ESCA (Electron Spectroscopy for Chemical Analysis) exists in zero (0) valence and monovalence, at least the surface of copper once reduced and immobilized reacts on a kind of active oxygen generated through the photo-catalytic action of the anatase-type titanium oxide and changes into a cuprous oxide. Thus, copper is decolorized in this process. The deodorizing properties, the abrasion resistance, and an anti-deposit or water scale resistance properties of the samples obtained here were evaluated.

[0068]

An evaluation on the deodorizing property was made by a method shown below using methyl mercaptan as an odor gas and by measuring  $R_{30}'$ . The  $R_{30}'$  can be obtained by the followings. After injecting 3 ppm of methyl mercaptan when it is dark into a glass vessel of 11L, it is left for a day as it is, so that a gas is fully absorbed into the sample. Then, after photo-dissociating the absorbed gas by irradiating lights thereupon for a day (the light source: 4-watt BLB fluorescent lamp to be disposed at the distance of 8 cm from the sample), the methyl mercaptan gas is newly injected into the vessel, so that the initial concentration thereof becomes 3 ppm. The  $R_{30}'$  can now be obtained by measuring the change of concentration after thirty (30) minutes when it is dark.

[0069]

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Evaluation on the abrasion resistance was made by comparing the changes of appearance after conducting sliding abrasion using a plastic eraser. Criteria for evaluation are shown below:

- ⊙: No change occurs after reciprocation of 40 times;
- : Cuts or scratches were made by sliding movement between 10 times and 40 times, and the photo-catalytic layer was removed;
- △: Cuts or scratches were made by sliding movement between 5 times and 10 times, and the photo-catalytic layer was removed; and
- X: Cuts or scratches were made by sliding movement of 5 times or less, and the photo-catalytic layer was removed.

Evaluation on the water deposit was made using the following apparatus. Namely, the sample was disposed, directing the surface of the sample forming a layer consisting of the photo-catalysts upwardly and irradiating light on the upper surface of the sample, wherein bath water collected in a public bath was continuously dripped on the sample while circulating the bath water. And, the surface of sample after fourteen (14) days was inspected and evaluation on the extent of sliminess produced and inorganic dirt was made. Evaluation criteria for the sliminess are shown below:

- ⊙: No sliminess cannot be acknowledged;
- : Slight sliminess can be felt;
- △: Sliminess has been produced; and
- X: Sliminess has been heavily produced.

Evaluation criteria for the inorganic dirt are shown below:

- ⊙: No inorganic dirt is produced;
- : Inorganic dirt is produced, but it can be easily wiped away, in a degree that a slight mark remains;
- △: Inorganic dirt has been produced, but it can be easily wiped away, in a degree that a mark remains a little; and
- X: Inorganic dirt has been produced, but it cannot be wiped away, in a degree of rubbing it out strongly.

The results are shown in Figs. 4 to 7, by thick points therein. By forming a mixed layer between the photo-catalysts made of anatase particles and copper (and cuprous oxide) and a siloxane resin on a surface of the base member, the abrasion resistance on the surface of the base member improves. BY making siloxane resin of the mixed layer be 20 wt.% or more, the evaluation turned to ⊙ or ○ (see Fig. 4). Also, the deodorizing properties improve by increasing the anatase particles. In the case where siloxane resin is 20 wt.% or less, the R30° showed 50% or more (see Fig. 5). Further,

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the evaluation on the inorganic dirt turned to ○ by adding siloxane resin by 20 wt.%. The evaluation on the sliminess also turned to ○ by adding siloxane resin by 20 wt.% to 30 wt.%. Thus, it was found that there is the anti-dirt effect. Furthermore, when measuring a wetting angle using a contact angle gauge, siloxane resin shows 50° in 20 wt.%, wherein a slight water-repellent action were observed compared with the following comparative examples.

**[0070]**

On the contrary, after applying a nitric acid dispersion liquid of titanium oxide sol onto the base member in the case of allowing the sample to carry only the photocatalysts made of anatase particles and copper (and cuprous oxide) (in the figure, siloxane resin: 0 wt.%; average particle size: 0.01 μm), the base member is baked at a temperature of 300 °C and thereafter, an aqueous solution of copper acetate is applied to the base member. In this case, when photo-reduction is conducted in the air (the light source: 20-watt BLB lamp; the distance from the light source to the sample: 10 cm; and the irradiation time: 15 min.), the anti-dirt or antifouling properties are not satisfactory because the dirt enters a gap between the anatase particles. The abrasion resistance is also not satisfactory because the adherence of the anatase particles to the base member is bad. Furthermore, when measuring a wetting angle using a contact angle gauge, it was 12° and a water-repellent property could be hardly acknowledged.

**[0071]**

After applying a liquefied material adding a hardening agent to a siloxane clear coat resin, having water repellent properties, diluted with propanol in advance to an aluminum substrate of 10 cm square in the case of allowing the sample to carry only siloxane resin and copper (in the figure, siloxane resin: 100 wt.%), the aluminum substrate is dried at a temperature of 150 °C. Then, an aqueous solution of copper acetate is applied onto this substrate. After this, there is no photo-activity even in the light irradiation (the light source: 20-watt BLB lamp; the distance from the light source to the sample: 10 cm; and the irradiation time: 15 min.). The deodorizing property R30° is bad (10%) because it cannot decompose the gas once absorbed. The anti-dirt or antifouling property is also bad.

**[0072]****(Embodiment 6)**

First, a liquified material adding a hardening agent to a siloxane clear coat resin, having a water repellent property, diluted by propanol in advance is applied to an aluminum substrate of 10 x 10 cm with a thickness of about 10 μm. The aluminum substrate was dried at a temperature of 150 °C. Next, nitric acid dispersion liquid of



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titanium oxide sol of which the average particle size is  $0.01 \mu\text{m}$  and a siloxane clear coat resin having a water repellent property are mixed at a predetermined weight ratio and diluted with propanol. After this, a liquid material added with a hardening agent was applied to the substrate and after application, the substrate was baked at a temperature of  $150^\circ\text{C}$  so as to solidify and then it was cooled. In addition, a copper acetate aqueous solution is applied to the substrate and a photo-reduction is conducted in the air (the light source: 20-watt BLB lamp; the distance from the light source to the sample: 10 cm; and the irradiation time: 15 min.), thereby the decolored sample was obtained. The film thickness of the mixed layer obtained in this manner is about  $0.3 \mu\text{m}$  and the film thickness of the intermediate siloxane resin layer was  $0.5 \mu\text{m}$ . The crystal of the titanium oxide was an anatase-type.

[0073]

The results are shown in white circles in Figs. 4 to 7. By providing the siloxane resin layer in the middle, the abrasion resistance was  $\bigcirc$  though an amount of siloxane resin of the mixed layer was 5 wt.%. Also, the deodorizing property showed a satisfactory result of more than 90% in the R30' though an amount of siloxane resin was 50 wt.%. Accordingly, if the siloxane resin layer is provided in the middle, it is possible to easily harmonize the two (2) properties mentioned above which show a reverse tendency relative to the amount of siloxane resin of the mixed layer. Also, the anti-dirt or antifouling properties are improved in particular on the sliminess mainly containing the organic components therein by adopting a structure which provides the siloxane resin layer in the middle and showed a satisfactory result ( $\odot$ ) in the amount of the siloxane resin of 5-50 wt.%.

[0074]

(Embodiment 7)

After applying glaze onto a base for forming a sanitary ware of 15 cm square, the base was baked at a temperature between  $1,100$  and  $1,200^\circ\text{C}$ . Further, anatase-type titanium oxide sol of which the average particle size is  $0.01 \mu\text{m}$  is applied to the base and baked at a temperature between  $900$  and  $1,000^\circ\text{C}$ , thereby immobilizing a thin film of a rutile-type titanium oxide on the base material for a sanitary ware. After this, an aqueous solution of silver nitride was applied onto the base material and by irradiating UV light thereon, silver was caused to deposit on the thin film of titanium oxide. Further, when the sample is left within a desiccator having an ozonizer (ozone concentration: 10 ppm) for about two (2) hours, then it was decolorized. Also, by bringing bacteria in contact with the sample for three (3) hours both when lights are irradiated and when it is dark, it was confirmed that only the bacteria of 10% or less of

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the original number of bacteria are live. Thus, the anti-bacterial properties showed a satisfactory result.

[0075]

(Embodiment 8)

After applying glaze on a base for forming a sanitary ware of 15 cm square, the base was baked at a temperature between 1,100 and 1,200 °C. Further, after applying a mixed liquid between sol of an anatase-type titanium oxide of which the average particle size is 0.01  $\mu\text{m}$  and an aqueous liquid of silver nitride onto the base, the base was baked to immobilize a thin film of a titanium oxide on the base material of the sanitary ware. In this case, the thin film shows brown color in the baking of 700 °C or less, but it was decolorized in the baking of 700 °C or more. It is understood that the surface of silver reacted on the components in the air. Also, when measuring the antibacterial property of the sample which was baked at a temperature of 850 °C and immobilized the thin film of anatase-type titanium oxide on the base material of the sanitary ware, it was confirmed that only the bacteria of 10% or less of the original number of bacteria is live, by bringing bacteria in contact with the sample for three (3) hours, both when lights are irradiated and when it is dark. Thus, the antibacterial properties showed a satisfactory result.

[0076]

(Embodiment 9)

After applying glaze on a base for forming a sanitary ware of 15 cm square, the base was baked at a temperature between 1,100 and 1,200 °C. Further, sol of an anatase-type titanium oxide of which the average particle size is 0.01  $\mu\text{m}$ , is applied on the base and baked at a temperature between 900 and 1,000 °C, thereby immobilizing a thin film of a rutile-type titanium oxide on the base material for a sanitary ware. After this, an aqueous solution of silver nitride is applied on the base material and by irradiating UV light thereon, silver was caused to deposit on the thin film of titanium oxide. When hydrogen peroxide water is applied on the thin film, the thin film was decolorized. Also, by bringing the bacteria in contact with the sample for three (3) hours both when lights are irradiated and when it is dark, it was confirmed that only the bacteria of 10% or less of the original number of bacteria are live. Thus, the antibacterial properties showed a satisfactory result.

[0077]

[Effect of the Invention]

By immobilizing the colored metal fine particles on the particles having photocatalytic activity, it is possible to maintain and improve the photo-catalytic activity high.

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Further, by allowing the colored metal particles to react on a solution or a gas to form achromatized (colorless) or whitened salts on at least the surfaces of the metal fine particles, it is possible to decolorize the film and fully utilize a design formed on the substrate.

**[Brief Explanation of the Drawings]**

Fig. 1 is a graph showing a color difference  $\Delta E$  between the embodiments of the present invention and the comparative examples;

Fig. 2 is a graph showing the photo-activity  $\Delta pH$  of the embodiments of the present invention and the comparative examples;

Fig. 3 is a graph showing an antibacterial property of the embodiments of the present invention and the comparative examples;

Fig. 4 is a view showing the embodiments of the present invention, and is a graph showing the relationship between an addition amount of a siloxane resin and abrasion resistance;

Fig. 5 is a view showing the embodiments of the present invention, and is a graph showing the relationship between an addition amount of a siloxane resin and deodorizing properties;

Fig. 6 is a view showing the embodiments of the present invention, and is a graph showing the relationship between an addition amount of a siloxane resin and an inorganic dirt; and

Fig. 7 is a view showing the embodiments of the present invention, and is a graph showing the relationship between an addition amount of a siloxane resin and the sliminess.

FIG. 3

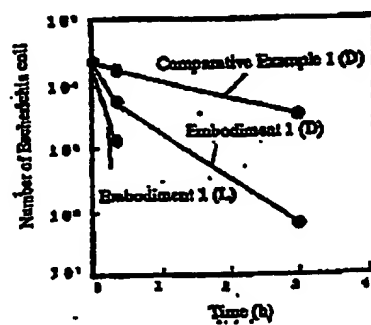


FIG. 4

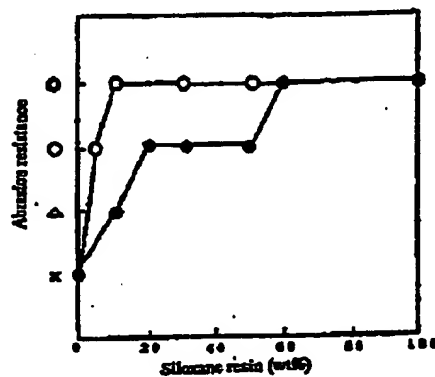


FIG. 5

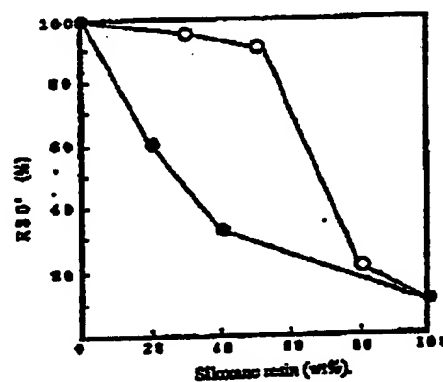


FIG. 6

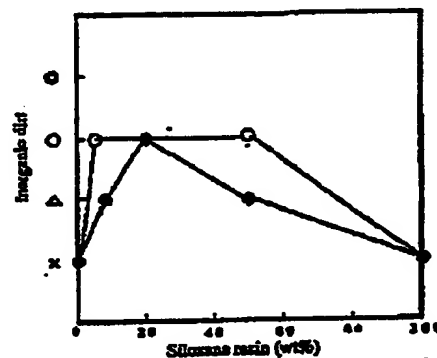
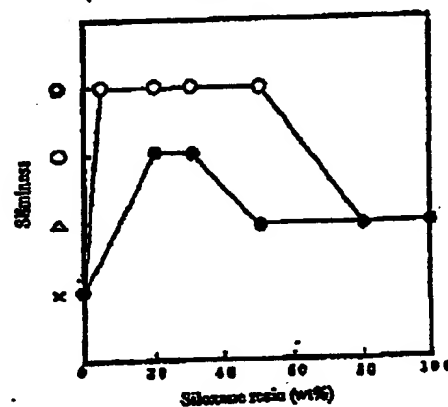


FIG. 7



jp07222928/pn

L1 ANSWER 1 OF 1 WPINDEX (C) 2002 THOMSON DERWENT  
ACCESSION NUMBER: 1995-224187 [29] WPINDEX  
CROSS REFERENCE: 1995-339428 [44]  
DOC. NO. CPI: C1995-103127  
TITLE: Multi functional photocatalytic material - used as an  
antibacterial sterilising agent for wall materials,  
tiles, ceramics etc..  
DERWENT CLASS: D22 J04 L02 P34 P73 Q43 Q45  
INVENTOR(S): CHIKUNI, M; HAYAKAWA, M; KIMURA, T; KITAMURA, A; KOJIMA,  
E; KUGA, T; MACHIDA, M; NAKAJIMA, Y; NORIMOTO, K; SAEKI,  
Y; WATANABE, T; CHIKUNI, Y; NAKASHIMA, Y  
PATENT ASSIGNEE(S): (TTOC) TOTO LTD  
COUNTRY COUNT: 60  
PATENT INFORMATION:

PATENT NO	KIND	DATE	WEEK	LA	PG	MAIN	IPC
WO 9515816	A1	19950615	(199529)*	JA	192	B01J035-02	
RW: AT BE CH DE DK ES FR GB GR IE IT KE LU MC MW NL OA PT SD SE SZ							
W: AM AT AU BB BG BR BY CA CH CN CZ DE DK EE ES FI GB GE HU KE KG KR							
KZ LK LR LT LU LV MD MG MN MW NL NO NZ PL PT RO RU SD SE SI SK TJ							
TT UA US UZ VN							
JP 07155598	A	19950620	(199533)		4	B01J021-06	
JP 07191011	A	19950728	(199539)		4	G01N031-00	
AU 9511998	A	19950627	(199541)			B01J035-02	
JP 07222928	A	19950822	(199542)		12	B01J035-02	<--
JP 07232080	A	19950905	(199544)		19	B01J035-02	
EP 684075	A1	19951129	(199601)	EN	129	B01J035-02	
R: AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE							
JP 08066635	A	19960312	(199620)		11	B01J035-02	
JP 08103488	A	19960423	(199626)		4	A61L009-01	
JP 08108075	A	19960430	(199627)		4	B01J035-02	
JP 08117606	A	19960514	(199629)		10	B01J035-02	
JP 08131524	A	19960528	(199631)		15	A61L009-01	
JP 08131834	A	19960528	(199631)		4	B01J023-72	
JP 08131842	A	19960528	(199631)		7	B01J035-02	
JP 08150197	A	19960611	(199633)		6	A61L009-01	
JP 08224481	A	19960903	(199645)		6	B01J035-02	
CN 1120819	A	19960417	(199745)			B01J035-02	
JP 10277403	A	19981020	(199901)		4	B01J035-02	
US 5853866	A	19981229	(199908)			B01J035-02	
US 6027797	A	20000222	(200017)			B01J035-02	
JP 2000227429	A	20000815	(200044)		4	G01N033-00	
US 6210779	B1	20010403	(200120)			B01J035-02	
TW 406031	A	20000921	(200127)			A61L009-00	
JP 2001121001	A	20010508	(200131)		4	B01J035-02	
US 6268050	B1	20010731	(200146)			B01J035-02	
JP 2001200627	A	20010727	(200158)		17	E04F013-14	
US 6294246	B1	20010925	(200158)			B32B003-26	
US 6294247	B1	20010925	(200158)			B01J021-04	
JP 3225761	B2	20011105	(200172)		4	B32B009-00	
JP 3246235	B2	20020115	(200206)		9	B01J035-02	
JP 3261909	B2	20020304	(200219)		10	B01J035-02	
JP 2002119865	A	20020423	(200243)#		17	B01J035-02	
JP 3309591	B2	20020729	(200256)#		17	B01J035-02	

## APPLICATION DETAILS:

PATENT NO	KIND	APPLICATION	DATE
WO 9515816	A1	WO 1994-JP2077	19941209
JP 07155598	A	JP 1993-310165	19931210
JP 07191011	A	JP 1993-348073	19931224
AU 9511998	A	AU 1995-11998	19941209
JP 07222928	A	JP 1994-337417	19941214
JP 07232080	A	JP 1994-254242	19940922
EP 684075	A1	WO 1994-JP2077	19941209
		EP 1995-902937	19941209
JP 08066635	A	JP 1994-310896	19941214
JP 08103488	A	JP 1994-274165	19940930
JP 08108075	A	JP 1994-282382	19941011
JP 08117606	A	JP 1994-297760	19941024
JP 08131524	A	JP 1994-271499	19941104
JP 08131834	A	JP 1994-311398	19941109
JP 08131842	A	JP 1994-313967	19941111
JP 08150197	A	JP 1995-134639	19950424
JP 08224481	A	JP 1995-322538	19951102
CN 1120819	A	CN 1994-191730	19941219
JP 10277403	A Div ex	JP 1994-282382	19941011
		JP 1998-93170	19941011
US 5853866	A	WO 1994-JP2077	19941209
		US 1995-501110	19951006
US 6027797	A Div ex	US 1995-501110	19951006
		US 1998-167324	19981007
JP 2000227429	A Div ex	JP 1993-348073	19931224
		JP 2000-55128	19931224
US 6210779	B1 Div ex	US 1995-501110	19951006
		US 1998-167326	19981007
TW 406031	A	TW 1994-112001	19941221
JP 2001121001	A Div ex	JP 1993-310165	19931210
		JP 2000-314691	19931210
US 6268050	B1 Div ex	US 1995-501110	19951006
		US 1998-167323	19981007
JP 2001200627	A Div ex	JP 1994-254242	19940922
		JP 2000-322232	19940922
US 6294246	B1 Div ex Div ex	WO 1994-JP2077	19941209
		US 1995-501110	19951006
		US 1998-167325	19981007
US 6294247	B1 Div ex Div ex	US 1994-501110	19940615
		WO 1994-JP2077	19941209
		US 1998-167327	19981007
JP 3225761	B2	JP 1994-282382	19941011
JP 3246235	B2	JP 1994-297760	19941024
JP 3261909	B2	JP 1994-337417	19941214
JP 2002119865	A Div ex	JP 1994-254242	19940922
		JP 2001-248877	19940922
JP 3309591	B2	JP 1994-254242	19940922

## FILING DETAILS:

PATENT NO	KIND	PATENT NO
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AU 9511998	A Based on	WO 9515816
EP 684075	A1 Based on	WO 9515816
US 5853866	A Based on	WO 9515816
US 6027797	A Div ex	US 5853866
US 6210779	B1 Div ex	US 5853866
US 6268050	B1 Div ex	US 5853866
US 6294246	B1 Div ex	US 5853866
US 6294247	B1 Div ex	US 5853866
JP 3225761	B2 Previous Publ.	JP 08108075
JP 3246235	B2 Previous Publ.	JP 08117606
JP 3261909	B2 Previous Publ.	JP 07222928
JP 3309591	B2 Previous Publ.	JP 07232080

PRIORITY APPLN. INFO: JP 1994-310896 19941214; JP 1993-310165

19931210; JP 1993-313061 19931214; JP  
 1993-313062 19931214; JP 1993-348073  
 19931224; JP 1994-143473 19940624; JP  
 1994-254242 19940922; JP 1994-271912  
 19940929; JP 1994-274165 19940930; JP  
 1994-282382 19941011; JP 1994-297760  
 19941024; JP 1994-271499 19941104; JP  
 1994-307173 19941104; JP 1994-311398  
 19941109; JP 1994-313967 19941111; JP  
 1993-351892 19931228; JP 1998-93170  
 19941011; JP 2000-55128 19931224; JP  
 2000-314691 19931210; JP 2001-248877 19940922  
 AU 9342168; CA 2101360; CA 2106510; EP 581216; EP 590477;  
 JP 01288321; JP 05012967; JP 05059562; JP 06198196; JP  
 06278241; JP 06293519

# REFERENCE PATENTS:

## INT. PATENT CLASSIF.:

### MAIN:

A61L009-01; B01J021-04; B01J023-72; B01J035-02;  
 B32B003-26; B32B009-00; E04F013-14; G01N031-00;  
 G01N033-00

### SECONDARY:

A61L009-18; A61L009-20; B01D053-36; B01D053-38;  
 B01D053-86; B01J013-00; B01J021-16; B01J023-00;  
 B01J023-04; B01J023-14; B01J023-42; B01J023-44;  
 B01J023-50; B01J023-62; B01J023-74; B01J023-835;  
 B01J023-89; B01J027-08; B01J037-02; B32B007-12;  
 B32B015-04; B32B017-06; C01G023-04; C01G023-053;  
 C03C017-34; C03C017-38; C04B041-83; C04B041-86;  
 C04B041-87; C04B041-89; E04B001-64; G01N021-78;  
 G01N031-16

### ADDITIONAL:

A61L009-00; B01J021-06; C04B041-85; G01N031-10

## BASIC ABSTRACT:

WO 9515816 A UPAB: 20011108

The following are claimed; (i) a multifunctional material having photocatalytic functions which comprises a photocatalyst layer on a base material. The photocatalyst layer has at least the surface exposed and the catalyst particles in the surface layer are combined with each other by potential energy. Alternatively the catalyst particles on the surface are combined by solid phase sintering; (ii) a multifunctional material of the same function as (i), wherein small particles are filled in the gaps formed between the catalyst particles and the electron-attracting particles from the catalyst particles and the small particles are fixed; (iii) a material as (ii), but wherein a binder layer is located between the base material and the photocatalyst layer; (iv) prepn. of the materials by; (a) forming a photo-catalyst layer on the base material; (b)

coating the surface with metal alkoxide or organic metal salt; (c) forming gaps between photocatalyst particles by drying and heating; (d) filling the gaps with small particles; (e) coating with aq. soln. contg. Cu, Ag, Zn, Fe, Co, Ni, Pd, Cu<sub>2</sub>O, and Pt ions; (f) fixing the metal particles obtd. by photoreduction; (5) prepn. of the material wherein the catalyst particles and the small particles are mixed in a sol. precursor or suspension state and the mixt. is coated to form a catalyst layer. One part of the lower layer of the photocatalyst is embedded by softening the thermoplastic base material, and finally the softened part is solidified; (6) prepn. of the material, similar to (5) wherein the catalyst particles are fixed by radiation contg. UV lights; (7) prepn. of the material wherein a thermoplastic binder sheet is formed on the base material, the photocatalyst layer is formed on the binder sheet and one part of the lower layer of the photocatalyst layer is embedded in the binder layer by softening the binder layer.

USE -The material has deodorant functions, antibacterial properties and anti-staining functions. It can be used for wall materials, tiles, sinks, anti-virus devices etc.

Dwg. 0/48

FILE SEGMENT:	CPI GMPI
FIELD AVAILABILITY:	AB
MANUAL CODES:	CPI: D09-A01C; D09-B; J04-E04; L02-A02A; L02-G01